

Letters to the Editor

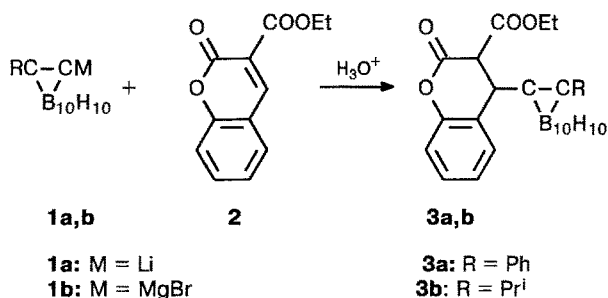
Conjugated addition of lithium and magnesium derivatives of *o*-carboranes to 3-carbethoxycoumarin

A. V. Kasantsev,* V. V. Butyaikin, E. A. Otrashchenkov, and Z. M. Muldakhmetov

E. A. Buketov Karaganda State University,
28 ul. Universitetskaya, 470074 Karaganda, Kazakhstan.
Fax: +7 (321 2) 744 950

It has been found previously^{1–4} that reactions of lithium and magnesium derivatives of *o*-carboranes with α,β -unsaturated ketones, benzylidenemalonate esters, and some other carbonyl compounds give products of 1,4-addition.

We continued the studies of the above-mentioned reactions and found that the reactions of lithium and magnesium derivatives of *o*-carboranes (**1a,b**) with 3-carbethoxycoumarin (**2**) give only products of conjugated addition, 3-carbethoxy-4-(*R*-*o*-carbonyl)-3,4-dihydrocoumarins (**3a,b**), in high yields, irrespective of the nature of solvent, the ratio between the reactants, and the order in which they are mixed.



When M = Li, the yields of products **3a** and **3b** are as high as 75–85 %, when M = MgBr, the yields do not exceed 60–65 %.

The structures of **3a** and **3b** were confirmed by IR and ¹H NMR spectra. The IR spectra of these compounds exhibit absorption bands at 1720, 1722; 1760; 2595, 2600; 2980, and 2982 cm⁻¹, typical of ester and lactone groups, B–H bonds of the carborane ring, and methine groups, respectively.

IR spectra were recorded on an UR-20 instrument, ¹H NMR spectra were obtained on a TESLA BS-587 instrument (80 MHz). The reactions were carried out in an argon atmosphere.

3-Carbethoxy-4-(phenyl-*o*-carboranyl)-3,4-dihydrocoumarin (3a). A. At ambient temperature, a benzene solution of 3-carbethoxycoumarin **2** (2.18 g, 0.01 mol) was added to a benzene solution of 1-phenyl-2-lithium-*o*-carborane **1a** (0.01 mol) prepared from phenyl-*o*-carborane (2.2 g, 0.01 mol) and BuLi (0.012 mol). The reaction mixture was stirred for 3 h (or more) at 20 °C, treated with dilute HCl, and extracted with benzene. The extract was dried with Na₂SO₄ and concentrated. The residue was crystallized from hexane to give 3.72 g (85 %) of **3a**, m.p. 198–199 °C (benzene–hexane).

B. At ambient temperature, compound **2** (2.18 g, 0.01 mol) was added to a tetrahydrofuran solution of 1-phenyl-2-bromomagnesium-*o*-carborane **1b** (0.01 mol), prepared from phenyl-*o*-carborane (2.2 g, 0.01 mol) and EtMgBr (0.013 mol). The reaction mixture was stirred for no less than 3 h at 20 °C, treated with dilute HCl, and extracted with benzene. The extract was dried with Na₂SO₄ and concentrated. The residue was crystallized from hexane to give 2.8 g (64 %) of **3a**. Found (%): C, 54.62; H, 7.21; B, 24.92; C₂₀H₂₆B₁₀O₄. Calculated (%): C, 54.92; H, 7.43; B, 24.71. IR (5 mg/600 mg

of KBr), ν/cm^{-1} : 2980 (C—H); 2595 (B—H); 1760, 1720 (C=O). ^1H NMR (C_6D_6), δ : 0.30 (t, 3 H, CH_2CH_3 , $J = 7.1$ Hz); 3.28 (q, 2 H, CH_2CH_3 , $J = 7.1$ Hz); 3.59 (d, 1 H, CH—CB, $J = 1$ Hz); 3.94 (d, 1 H, CH—CH, $J = 1$ Hz); 7.1–7.5 (m, 9 H, Ar).

3-Carboethoxy-4-(isopropyl-*o*-carboranyl)-3,4-dihydrocoumarin (3b). A. Compound **3b** was prepared from 1-isopropyl-2-lithium-*o*-carborane **1a** (0.01 mol) and compound **2** (0.01 mol) similarly to **3a**, procedure A, yield 3.2 g (79 %), m.p. 188–189 °C (benzene–hexane).

B. Compound **3b** was prepared from 1-isopropyl-2-bromomagnesium-*o*-carborane **1b** (0.01 mol) and compound **2** (0.01 mol) similarly to **3a**, procedure B, yield 2.26 g (56 %). Found (%): C, 50.21; H, 6.77; B, 26.39. $\text{C}_{17}\text{H}_{28}\text{B}_{10}\text{O}_4$. Calculated (%): C, 50.49; H, 6.93; B, 26.73.

IR (5 mg/600 mg of KBr), ν/cm^{-1} : 2982 (C—H); 2600 (B—H); 1760, 1722 (C=O). ^1H NMR (C_6D_6), δ : 0.45 (t, 3 H, CH_2CH_3 , $J = 7.1$ Hz); 0.87 (d, 6 H, $(\text{CH}_3)_2\text{CH}$, $J = 7$ Hz); 2.21 (m, 1 H, $(\text{CH}_3)\text{CH}$, $J = 7.1$ Hz); 4.07 (s, 2 H, CH—CH); 6.4–6.8 (m, 4 H, Ar).

References

1. L. I. Zakharkin and A. V. Kazantsev, *Zh. Obshch. Khim.*, 1966, **36**, 944 [*J. Gen. Chem. USSR*, 1966, **36** (Engl. Transl.)].
2. L. I. Zakharkin and A. V. Kazantsev, *Zh. Obshch. Khim.*, 1967, **37**, 554 [*J. Gen. Chem. USSR*, 1967, **37** (Engl. Transl.)].
3. L. I. Zakharkin, A. V. Kazantsev, B. T. Ermaganbatov, and A. P. Fonshtein, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1975, 710 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1975, **24** (Engl. Transl.)].
4. A. V. Kazantsev, Yu. A. Kazantsev, and V. V. Butyaikin, *Metalloorg. Khim.*, 1992, **3**, 570 [*J. Organomet. Chem. USSR*, 1992, **3** (Engl. Transl.)].

Received January 10, 1995;
in revised form May 11, 1995

Cyclocondensation of benzylideneanilines with 2-(thiazolyl-4)cyclohexane-1,3-dione hydrochlorides. A novel reaction in the series of Schiff's bases

O. V. Gulyakevich* and A. L. Mikhail'chuk

Institute of Bioorganic Chemistry, Belarus' Academy of Sciences,
5/2 ul. Zhodinskaya, 220141 Minsk, Belarus'.
Fax: +7 (017 2) 637 274

The formation of a pyridine ring through condensation of various β -di- and β,β' -tricarboxyl compounds with amines, enamines, or azomethines has acquired wide use in preparing derivatives of both pyridine itself and a number of fused heterocyclic compounds incorporating pyridine rings.^{1–3} However, no data concerning synthetic application of 2-hetaryl(aryl)-1,3-dicarbonyl compounds have been published in the literature.

While continuing studies on reactions of Schiff's bases with β -dicarbonyl compounds and their enol derivatives,^{4–6} we found that benzylideneanilines react with 2-thiazolyl derivatives of cyclic 1,3-diketones to give thiazolo[c]quinoline derivatives.

For example, boiling an equimolar mixture of benzylideneanilines (**1a,b**) with 2-(2-aminothiazolyl-4)cyclohexane-1,3-dione hydrochlorides (**2a,b**) in alcohols or glacial acetic acid yields little known thiazolo[c]quinoline hydrochlorides (**3a,b**), which are difficult to obtain.

These compounds are of much interest, first, as compounds possessing potential biological activity and, second, as intermediate compounds in synthesis of biologically active quinoline derivatives, including some quinoline alkaloids. There are weighty grounds to believe that this reaction is rather general and can be extended to acyclic 2-hetaryl-1,3-dicarbonyl compounds and used, for example, in the synthesis of thiazolo[c]pyridine derivatives. The mechanism of this reaction, the limits of its applicability, and optimization of its conditions are being currently studied.

IR spectra were recorded on a UR-20 instrument. UV spectra were measured on a Specord M-400 spectrophotometer.

Benzylideneanilines **1a,b** used in the study were prepared by the general procedure,⁷ and 2-(thiazolyl-4)cyclohexane-1,3-diones **2a,b** were synthesized by the procedure⁸ described by us previously. The course of the reactions was monitored by TLC on Silufol UV-254 plates using a 9:1 chloroform–